(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 010 871
A1

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: 79302079.3

(22) Date of filing: 02.10.79

(51) Int. Cl.³: B 01 J 39/22, C 08 B 3/12, C 08 B 3/24

(30) Priority: 11.10.78 GB 4014578

(43) Date of publication of application: 14.05.80 Bulletin 80/10

(84) Designated Contracting States: AT BE CH DE FR GB IT LU NL SE

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(84) Designated Contracting States: GB

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(84) Designated Contracting States: BE CH DE FR IT LU NL SE AT

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(54) **Carboxylated cellulose ion-exchange materials, process for their preparation and their use in removing heavy metal ions from aqueous solutions.**

(57) A process for preparing a carboxylated cellulose ion-exchange material comprises heating a mixture of cellulose and citric, isocitric or aconitic acid at 100–160°C while continuously removing water, and then treating the product with aqueous alkali at a pH of 8 to 11 to hydrolyse cross-linked acid residues. Carboxylated cellulose ion-exchange materials having an ion-exchange capacity towards cupric ions of 1.5 to 3.5 milliequivalents per gram and their use in removing heavy-metal ions from aqueous solutions are claimed. Citrated sawdust is a preferred product useful in industrial effluent treatment and precious metal recovery.

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This invention relates to ion-exchange materials and is particularly concerned with carboxylated cellulose products and their salts having ion-exchange properties and with a process for their preparation. The products have particular application in scavenging heavy metal ions from aqueous solution for example in effluent treatment and in precious metal recovery.

Cellulose esters containing free carboxyl groups are well known, in particular the esterification of cellulose with citric acid has been described as a method of textile finishing to improve crease resistance in cellulosic fabrics (Gagliardi and Shippee: American Dyestuff Reporter, April 15, 1963, 74). That such materials exhibited ion-exchange properties was noted. U.S. Patent No. 2759787 also describes the preparation of insoluble cellulose citrates by the reaction of citric acid and cellulose. The products are said to be useful as absorbents for high molecular weight materials. Such products have not, however, found general application as ion-exchange materials because of their low ion-exchange capacity.

We have now discovered that when cellulose is reacted with citric, isocitric or aconitic acid by a particular process, as will be hereinafter described, and the product is subjected to a hydrolysis step under controlled conditions as will also be described, water-insoluble products are obtained having a high degree of incorporation of acid and a high proportion of free carboxyl groups. The products have excellent stability together with a high ion-exchange capacity.

We have further discovered that the products exhibit a selectivity for heavy-metal ions, e.g. copper, nickel and zinc, in the presence of calcium ions which makes the product of particular value, for example, in the treatment of industrial effluents.

Thus, according to the invention, a process for preparing a carboxylated cellulose ion-exchange material comprises (a) heating a mixture of cellulose and citric, isocitric or aconitic acid containing from 30 to 70% by weight of the acid, at a temperature in the range from 100 to 160°C while continuously removing water therefrom until the cellulose has reacted with at least 20% of its own weight of acid; and (b) treating the product with aqueous alkali maintained at a pH of from 8 to 11 until the ion-exchange capacity of the product relative to cupric ions is at least 1.5 milliequivalents per gram. Also, according to the invention, there is provided a carboxylated cellulose ion-exchange material having an ion-exchange capacity towards cupric ions of 1.5 to 3.5 milliequivalents per gram.

Various forms of cellulose may be used as starting material for the process, thus, for example refined cellulose powder may be used or crude forms of cellulose such as wood-pulp, sawdust, wood-chips or waste newsprint. Sawdust and waste-newsprint are preferred sources of cellulose on grounds of cost and because of the desirable ion-exchange properties of the products obtained from these materials.

The amount of citric, isocitric or aconitic acid used may vary between 30 and 70% of the total weight of the mixture of cellulose and acid before heating. The use of smaller amounts of acid leads to products having too low an incorporation of acid to give products with useful ion-exchange capacities. Higher levels of acid may be employed but we have found that in practice there is little advantage to be gained when the acid content of the mixture exceeds 60%. For optimum incorporation of acid the preferred amount of acid in the mixture is from 40 to 60%. Citric acid is a preferred acid for use in the process. The citric acid may be used as anhydrous citric acid or in the form of its monohydrate. It is also possible to use crude citric acid obtained directly from fermentation broths.

The mixture of cellulose and citric, isocitric or aconitic acid may be prepared in a number of ways. For example, the mixture can be prepared using cellulose and the acid in powder form and using conventional solid/solid mixing techniques. Alternatively, an aqueous solution of the acid may be sprayed onto cellulose in a suitably agitated dryer. Preferably, however, the cellulose, sawdust or newsprint etc. is dispersed in an aqueous solution of the acid to form a slurry. The slurry is stirred and the wet mass is then dried, for example, by spray drying or by drying on trays in an oven or on a heated roller. The product may be ground or milled as required to give a free-flowing powder.

It is preferred for carrying out the invention that the moisture content should be low prior to and during the heating stage of the process. The mixture should contain less than 5% water and preferably less than 2% water by weight of the mixture. The mixture of cellulose and acid may therefore have to be dried e.g. by heating at a temperature below 100°C to reduce its water content to below 5% by weight before heating, in the range 100 to 160°C is begun. Water is formed by reaction between the carboxyl groups of the acid and the hydroxyl groups of the cellulose and this must be removed continuously from the mixture during heating. This may be achieved by carrying out the heating step under reduced pressure e.g. at below 150 mm of mercury, preferably below 50 mm mercury. The pressure may be maintained at the required level by means of a vacuum pump or steam ejector. Alternatively a purge of air or nitrogen may be used to remove water vapour from the reaction vessel as it is formed. Operating under vacuum or with a nitrogen purge has the further advantage of reducing oxidation due to the presence of air which can lead to discolouration of the product especially at higher temperatures in the range.

The temperature used during the heating stage is in the range 100° to 160°C, a temperature of 130 - 150°C being generally preferred as lower temperatures lead to prolonged reaction times while higher temperatures tend to lead to degradation of the product. Lower temperatures in the range may be employed with aconitic acid whereas reactions with citric acid generally require higher temperatures.

The period of time required to achieve sufficient reaction between the cellulose and the acid will naturally depend upon the nature of the starting material, the proportion of acid present and the type of apparatus used for the heating step as well as the actual temperature employed. In practice, the heating is continued for a time sufficient to ensure that the cellulose has reacted with at least 20% of its own weight of acid. This may be determined from the weight gain of the reaction product after washing to remove unreacted citric acid, and may be estimated at any point during the heating process by removing a sample of the product and measuring the proportion of water-soluble material remaining in the mixture. The heating may be terminated when the required amount of the acid initially present has reacted but is preferably continued until there is no further reaction. The time taken to achieve this will vary with the proportion of acid initially present, mixtures containing higher levels of acid reacting faster initially but taking longer to reach the stage where there is no further incorporation of acid. In practice, however, we have found that when a temperature of 140°C is employed and citric acid is used at levels of 40 - 60% a period of 2 to 6 hours is generally sufficient to achieve maximum incorporation of the citric acid. The amount of unreacted acid remaining will naturally depend on the proportion initially present; at higher initial acid contents it is to be expected that there will be more unreacted acid.

We have found, however, that under appropriate conditions, even with a mixture initially containing 60% citric acid it is possible to incorporate well over half of the citric acid into the cellulose to give citrated cellulose products with a citric acid content of up to 50% of the weight of the product.

The presence of a catalyst during the heating stage has been found to be beneficial and enables the higher levels of acid incorporation to be achieved as well as giving products with improved ion-exchange capacities. The use of a catalyst is especially valuable when the cellulose source is sawdust or newsprint. Suitable catalysts are acidic materials e.g. phosphoric acid or sulphamic acid or preferably aluminium sulphate. The catalyst may be added to the mixture at a level of from 0.1 to 1% based on the total weight of the mixture but, in the case of aluminium sulphate, a level of 0.2% is preferred.

If desired, the product obtained after the mixture has been heated as described may be washed with water to remove unreacted acid, catalyst and any water soluble by-products. This washing step may, however, be omitted, particularly where the residual levels of acid are low, the product being treated directly with alkali in the next stage of the process.

The hydrolysis step is an essential part of the process of the invention and gives a product having a much increased ion-exchange capacity towards heavy metal ions. It is believed that during the hydrolysis step cross-linked acid residues are hydrolysed and a product results wherein each acid moiety is bound to the cellulose by a single ester bond while the other two carboxyl groups are free. Thus, depending on the amount of acid incorporated into the cellulose, products having ion-exchange capacities of the order of 1.5 to 3.5 milliequivalents per gram (measured as cupric ions) may be achieved.

The hydrolysis step is generally performed by stirring the product from the heating stage in dilute alkali at a pH of 8 to 11. Suitable alkalis are the salts of weak acids such as sodium bicarbonate, sodium carbonate, sodium tetraborate, sodium acetate or ammonium acetate. Alternatively a strong base such as sodium hydroxide may be used, the pH of the solution being maintained in the desired range by using an automatic titration apparatus (pH-stat). The optimum pH range is 8.5 to 9. If the pH of the solution is allowed to rise too far, acid is lost from the product. Preferred alkalis are sodium carbonate and sodium bicarbonate, the pH of their aqueous solutions falling naturally into the desired pH range. After the initial uptake of sodium ions there is a slower uptake believed to be due to hydrolysis of cross-linked acid residues and this correlates with the increase in the ion-exchange capacity of the product for cupric ions.

The pH is maintained in the desired range by the addition of further sodium carbonate or bicarbonate if required, but generally a sufficient excess (e.g. a 10% excess) can be estimated based on the citric acid content of the material.

The alkali treatment is continued until the ion-exchange capacity of the product towards copper ions exceeds 1.5 milli-equivalents/g but is preferably continued until there is no further increase in the ion-exchange capacity of the product. This is generally indicated when there is no further uptake of alkali from solution. The amount of alkali in solution is readily determined by titration of a sample with an acid using an appropriate indicator. In practice we have found that, at room temperature, a period of from 1 to 24 hours is generally sufficient. Naturally the reaction time may be shortened by heating but care must be taken to ensure that the hydrolysis does not lead to loss of acid from the product. The product is then collected by filtration, washed and dried to give the carboxylated cellulose as the sodium salt. Naturally other alkali metal salt forms may be prepared using the appropriate alkali.

The ion-exchange capacity of the product for copper ions is assessed by weighing out a sample of the product and adding it to a known volume of a solution containing a known concentration of copper e.g. copper sulphate at 500 p.p.m.

The suspension is stirred for 2 hours and filtered. The solid is washed and the filtrate made up to a known volume and the residual copper concentration is measured by a standard analytical technique e.g. by gravimetric determination or by atomic absorption spectroscopy. The quantity of copper absorbed by the product is calculated from the amount of copper remaining in solution. The citrated celluloses having ion-exchange capacities for heavy-metal ions of from 1.5 to 3.5 milliequivalents/g prepared by the process of this invention are novel products having ion-exchange capacities not previously attainable in citrated cellulose products.

The carboxylated cellulose ion-exchange materials of the invention are weakly acidic ion-exchange materials of value in a variety of applications, e.g. in antibiotic recovery, but we have found that the materials are capable of removing heavy-metal ions e.g. copper, zinc, nickel, cadmium, mercury, silver etc. from aqueous solutions and are thus particularly useful in such operations as scavengers for heavy-metal ions in industrial effluents, in various water-treatment processes and in the recovery of precious metals e.g. in the recovery of silver from silver containing residues. We have further discovered that the carboxylated cellulose materials of the invention exhibit a selectivity for heavy-metal ions in the presence of calcium ions. This makes the products of particular value in hard water areas or in treating, for example, electroplating effluents where the addition of lime is used to reduce levels of metal ions.

Thus the invention also provides a method of removing heavy-metal ions from aqueous solutions which comprises contacting the solution with the carboxylated cellulose ion exchange materials of the invention. (PLC. 279)

The ion-exchange materials which have been used to remove heavy metal ions may be readily regenerated by treatment with dilute acid, for example, by stirring with 5% hydrochloric acid or 0.8% sulphuric acid for 2 hours, to give the product in the free acid form. Reconversion to the salt form (e.g. the sodium salt) may readily be achieved by stirring with sodium bicarbonate as previously described or by gradual addition of the calculated quantity of sodium hydroxide. Other salt forms may be prepared by addition of the appropriate base, e.g. the ammonium salt may be prepared by addition of aqueous ammonium hydroxide. The material has excellent stability and may be recycled indefinitely with no loss of ion-exchange capacity. A further desirable and unexpected property of the carboxylated cellulose ion-exchange materials of the invention is their very fast ion-exchange kinetics. We have found that, particularly the products derived from cellulose powder or newsprint, have an exchange kinetic half-life of 10 - 20 seconds. This makes such products of particular value in column and flow applications and where large volumes of effluent are being treated.

The process for the preparation of the carboxylated cellulose ion-exchange materials and their use in ion-exchange processes is further illustrated by the following Examples:-

EXAMPLE 1

(A) A mixture of waste newsprint (1.00 kg), citric acid monohydrate (1.50 kg) and aluminium sulphate hydrate (5 g) was stirred with water (10 litres) in a stainless steel container. After several hours the wet mass was dried in a forced air oven at 70°C to a water content of less than 2% by weight and the product was milled and sieved through a 1 mm mesh sieve.

(B) A proportion of the product from (A) (600 g) was stirred and heated under a pressure of 110 mm mercury (maintained by a vacuum pump) in a 5 litre vessel. A temperature of 140°C was reached after 6 hours and was maintained for a further 2 hours. At the end of this period 73.2% of a small sample of the product was found to be insoluble in water. The reaction product (544 g) was suspended in water and after 3 hours the product was collected by filtration, washed with a little water and dried. The yield (398 g) indicated that the cellulose had reacted with 65% of its weight of citric acid.

(C) The residue from (B) was suspended with stirring in water (1 litre) and a solution of sodium bicarbonate (300 g) in water (3 litres) was added in 10 equal increments at 10 minute intervals. A further 300 g sodium bicarbonate was then added and the suspension was stirred for a further 3 hours and allowed to stand overnight at room temperature. The product was collected by filtration, washed with water (3 x 1.5 litres) and dried in a forced air oven at 85°C for 36 hours. The final product (397 g) had an ion-exchange capacity towards cupric ions of 99.3 mg copper/g (3.13 milliequivalents/g).

EXAMPLE 2

Waste newsprint (10.0 g) was macerated in 200 ml deionised water containing 10 g citric acid monohydrate for 20 minutes. The mixture was dried at 70°C overnight and the product milled and sieved through a 100 mesh screen. The fine powder was reacted at 145°C under a vacuum of 50 mm mercury for four hours to give a product (19.5g) which was 87% insoluble in water. The product was cooled and suspended with stirring in 1M sodium bicarbonate (150 ml) for 1 hour. After filtration the product was washed until neutral and dried at 75°C. The product (17.1 g) had a copper ion-exchange capacity of 2.4 milliequivalents/g.

EXAMPLES 3-8

The general procedure of Example 2 was followed using various proportions of newsprint and citric acid. Heating was performed under a vacuum of 50 mm mercury at various temperatures and for various times. The following Table gives the conditions used, the yield and degree of insolubility of the product after the heating stage and the ion-exchange capacity of the product (relative to cupric ions) after the hydrolysis stage.

Example	Newsprint %	Citric Acid %	Temperature °C	Time hours	Yield %	% Insoluble	Ion exchange capacity after hydrolysis milliequivalents/g
3	40	60	140	2.0	95.8	53.5	2.62
4	40	60	150	2.0	94.3	55.0	2.84
5	50	50	150	2.5	92.5	65.0	2.75
6	50	50	160	2.5	80.0	78.0	2.87
7	60	40	140	2.5	95.4	79.0	2.33
8	60	40	160	2.0	85.2	90.5	2.60

(PLC. 279)

EXAMPLE 9

(A) Sawdust (20 g) was added to a solution of citric acid monohydrate (20 g) and aluminium sulphate hydrate (0.08 g) in water (400 ml). The mixture was heated to boiling and stirred for 2 hours until it had the consistency of a paste, it was then dried in an oven at 90°C for 16 hours to a moisture content of less than 2%.

(B) 15 g of the product from (A) was stirred and heated in a glass flask at 150°C under a pressure of 50 mm mercury for 2 hours to yield 11.4 g of a product 95.6% insoluble in water indicating that the sawdust had reacted with 44% of its weight of citric acid.

(C) The product from (B)(10.25 g) was suspended in 300 ml of 1M sodium bicarbonate and stirred overnight at room temperature. The solid material was collected by filtration, washed several times with water and dried at 60°C in a forced air oven for 48 hours. The product (9.85 g) had a copper ion-exchange capacity of 2.85 milliequivalents/g .

EXAMPLES 10-13

The procedure of Example 9 was followed using various proportions of sawdust and citric acid and heating for 3 hours at 140°C and 50 mm mercury pressure. The following Table gives the proportions used, the yield and the degree of insolubility of the product after the heating stage and the ion-exchange capacities of the products (relative to cupric ions) both before and after the hydrolysis stage.

Example	Sawdust g	Citric acid monohydrate g	aluminium sulphate g	Yield g	% Insoluble	Cu^{2+} capacity, milliequivalents/g.	
						Before Hydrolysis	After Hydrolysis
10	7.0	3.0	0.02	8.4	100	0.24	1.76
11	6.0	4.0	0.02	7.8	96	0.39	2.28
12	5.0	5.0	0.02	7.9	78	0.50	2.79
13	4.0	6.0	0.02	7.2	89	0.50	3.10

(PLC. 279)

EXAMPLE 14

The procedure of Example 12 was followed but the heating stage was performed under vacuum at a temperature of 117°C for 20 hours to give 9.3 g of product 80% insoluble in water. After hydrolysis the product had a copper ion-exchange capacity of 2.5 milliequivalents/g.

EXAMPLE 15

A mixture of cellulose powder (6.5 g) and citric acid (hydrate) (3.5 g) and aluminium sulphate 0.02 g was slurried with water (200 ml) and after 30 minutes the wet mass was dried at 70°C overnight to a moisture content of less than 2%. The product was milled and sieved through a 100 mesh screen. The fine powder was heated in a glass flask at 140°C on an oil bath at a pressure of 50 mm mercury (maintained by a vacuum pump), for a period of 3 hours to give a product (9.9 g) which was 85% insoluble in water.

The product was washed with water (2 x 200 ml) and suspended in 300 ml 1M sodium bicarbonate. The mixture was stirred for 16 hours at room temperature and the product collected by filtration, washed several times with water and dried at 60°C in a forced air oven. The product (8.0 g) had an ion-exchange capacity for cupric ions of 1.65 milliequivalents/g.

EXAMPLES 16-18

The procedure of Example 15 was followed using the following catalysts to give products with the ion-exchange capacities relative to copper-ions as shown. In the absence of a catalyst the product has a Cu^{2+} capacity of 1.1 milliequivalents/g.

Example	Catalyst	weight g	Cu^{2+} capacity milli-equivalents/g
16	NH_2SO_3H	1.0	1.8
17	NH_2SO_3H	0.5	1.65
18	H_3PO_4 (90%)	0.2	1.5

EXAMPLE 19

The general procedure of Example 2 was followed but using newsprint (4 g) and a quantity of crude, cell free fermentation broth containing citric acid (6 g).

After reaction at 135°C and 50 mm mercury pressure for 2.5 hours the product was hydrolysed with sodium bicarbonate as described in Example 2 to give a final product having an ion-exchange capacity for cupric ions of 2.74 milli-equivalents/g.

EXAMPLE 20

A mixture of cellulose powder (4 g) and aconitic acid (7.1 g of 84% purity) was slurried with water, dried and heated at a temperature of 145°C under a pressure of 50 mm mercury as described in Example 15, to give a product (7.42 g) which was 65 % insoluble in water. The product was washed and hydrolysed as before to give a product with an ion-exchange capacity for cupric ions of 3.13 milliequivalents/g.

EXAMPLE 21

(A) Sawdust (80 g) was added to a solution of citric acid monohydrate (125 g) in demineralised water (100 ml) and stirred to a smooth consistency. The wet product was dried in trays in a forced air oven at 90°C to a moisture content of less than 5%.

(B) 56.9 g of the product from (A) was reacted at 120-138°C in a rotary vacuum drier under a pressure of 66 mm mercury for 2 hours to yield 52.1 g of a product which was 63.7% insoluble in water indicating that the sawdust had reacted with 44% of its weight of citric acid.

(C) The crude product from (B) was suspended in demineralised water (400 ml) and stirred for 2 hours. The product was collected by filtration, suspended in a solution of sodium carbonate (24.6 g) in water (283 ml) and stirred at room temperature for 2 hours. The product was collected by filtration, washed with water until free of residual sodium carbonate and dried in a vacuum oven overnight. The final product (35.0 g) had an ion-exchange capacity towards cupric ions of 3.04 milliequivalents per gram.

EXAMPLE 22

Sawdust (10.0 g) citric acid (15.0 g) and water (60 ml) were mixed together and the wet mass dried overnight in an oven at 70°C. The product was heated in an oven at 140 - 150°C for 3 hours under atmospheric pressure using a slow bleed of air to remove water vapour formed during the reaction.

The product (21.7 g) was washed with water (50 ml) and the residue suspended in 1M sodium bicarbonate solution (650 ml) and stirred at room temperature for several hours. The product was collected by filtration, washed with water until free of sodium bicarbonate and dried at 70°C. The final product (13.0 g) had an ion exchange capacity for cupric ions of 2.93 milliequivalents per gram.

EXAMPLE 23

The use of the citrated cellulose products as ion-exchange materials is illustrated by the following tests : Various synthetic rinse waters were made up from laboratory reagents (usually metal chlorides) dissolved in deionised water. The citrated cellulose product of Example 15 was added to 50 ml of the rinse water and stirred for one hour, the solution filtered and the residual metal ion concentrations were measured by atomic absorption spectroscopy on the filtrates. The amount of resin used was calculated as 110% of the measured copper ion-exchange capacity based on the total weights of metals in solution.

Similar results were obtained with the products derived from newsprint and sawdust.

Synthetic Rinse water A   pH 4.0

	Cu^{2+}	Zn^{2+}	Ni^{2+}	Cd^{2+}
Initial concentration of metal ions in solution (ppm)	50	50	30	30
Final concentration after treatment with citrated cellulose (176 mg)	0.6	3.7	4.3	0.2

Synthetic Rinse water B   as A but adjusted to pH 5.9 with sodium carbonate

	Cu^{2+}	Zn^{2+}	Ni^{2+}	Cd^{2+}
Initial concentration of metal ions in solution (ppm)	50	50	30	30
Final concentration after treatment with citrated cellulose (176 mg)	0.6	2.5	0.3	0.3

Synthetic Rinse water C as A but adjusted to pH 10 with 10% calcium hydroxide and filtered

	Cu^{2+}	Zn^{2+}	Cd^{2+}
Initial concentration of metal ions in solution (ppm)	0.5	0.5	0.3
Final concentration after treatment with citrated cellulose (180 mg)	0.0	0.0	0.0

Synthetic Rinse water D pH 4.9

	Cu^{2+}	Zn^{2+}
Initial concentration of metal ions in solution (ppm)	400	10
Final concentration after treatment with citrated cellulose (500 mg)	17.5	1.8

Synthetic Rinse water E   pH 5.5
contains calcium (200 p.p.m.)

	Cu^{2+}	Ni^{2+}	Cd^{2+}
Initial concentration of metal ions in solution (ppm)	20	10	10
Final concentration after treatment with citrated cellulose (44 mg)	1.7	8.8	6.5

Synthetic Rinse water F

	Hg^{2+}
Initial concentration of metal ions in solution (p.p.m.)	5.00
Final concentration after treatment with citrated cellulose (25 mg)	0.21

EXAMPLE 24

A 1 litre sample of a commercial electroplating effluent was passed down a column (1.5 x 18.0 cm) containing 5.0 g of the citrated sawdust product of Example 21 at a flow rate of 7.5 ml/min. The composition of the eluate was monitored at 250 ml fractions and the results are shown in the Table below:

	Concentration ppm							
	Vol.ml	pH	Cu	Ni	Cd	Zn	Fe	Ca
Input	1000	3.7	10.0	91.0	1.7	48.0	26.0	50.0
Eluate 1	250	6.7	2.2	0.0	0.0	0.0	0.0	0.0
2	250	6.4	2.2	0.0	0.0	0.0	0.0	0.0
3	250	6.1	1.9	0.6	0.0	0.3	0.0	13
4	250	5.8	1.9	9.9	0.3	8.0	1.0	100

EXAMPLE 25

A sample of "silver mud" from a mirrormanufacturer containing residual silver, silver oxide and dextrose was dried, dissolved in 25% nitric acid at 70°C and the solution filtered and the pH adjusted to 6.1 with 0.1M sodium hydroxide. The solution was passed down a 1.5 cm diameter column containing the citrated sawdust product of Example 21 (3.75 g). The column was washed with water and the absorbed silver (1.28 g as Ag^{+}) was recovered quantitatively by elution with 1M nitric acid to give silver nitrate of 99.2% purity by Volhard titration.

CLAIMS

1. A process for preparing a carboxylated cellulose ion exchange material comprising (a) heating a mixture of cellulose and citric, isocitric or aconitic acid containing from 30 to 70% by weight of the acid, at a temperature in the range from 100 to 160°C while continuously removing water therefrom until the cellulose has reacted with at least 20% of its own weight of acid; and (b) treating the product with aqueous alkali maintained at a pH of from 8 to 11 until the ion-exchange capacity of the product relative to cupric-ions is at least 1.5 milliequivalents per gram.

2. A process as claimed in claim 1 wherein the cellulose is heated with citric acid.

3. A process as claimed in claim 1 or 2 wherein the cellulose is in the form of sawdust or waste-newsprint.

4. A process as claimed in any preceding claim wherein the acid is present in an amount of 40 to 60% of the weight of the mixture.

5. A process as claimed in any preceding claim wherein the mixture is heated at a temperature in the range 130 - 150°C.

6. A process as claimed in any preceding claim wherein the mixture is dried to a moisture content of less than 5% prior to the heating stage of the process.

7. A process as claimed in any preceding claim wherein water is continuously removed during the heating stage of the process by carrying out the heating step under reduced pressure.

(PLC. 279)

8. A process as claimed in any preceding claim wherein the product from the heating stage is treated with aqueous sodium carbonate or sodium bicarbonate at a pH of from 8.5 to 9.0.

9. A carboxylated cellulose ion-exchange material having an ion-exchange capacity towards cupric ions of 1.5 to 3.5 milli-equivalents per gram.

10. A method of removing heavy-metal ions from aqueous solutions which comprises contacting the solution with a carboxylated cellulose ion-exchange material as claimed in claim 9 or as prepared by a process as claimed in any one of claims 1 to 8.

(PLC. 279)

European Patent Office

EUROPEAN SEARCH REPORT

0010871

Application number
EP 79 30 2079

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
D	US - A - 2 759 787 (TOUEY) * Column 1, lines 67-72; column 2, lines 1-72; column 3, lines 1-75; column 4, lines 1-34 * --	1,2,5
	US - A - 3 097 051 (WADE) * Column 3, lines 37-55; column 8, lines 30-62 * --	1
	DE - B - 1 209 552 (ARMOUR PHARMACEUTICAL CO.) * Column 3, lines 27-34 * --	1,2
A	US - A - 2 505 561 (McINTIRE)	
A	US - A - 3 703 438 (DOUGALEV)	
A	US - A - 2 664 397 (HUTCHINSON) ----	

CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)

B 01 J 39/22
C 08 B 3/12
3/24

TECHNICAL FIELDS SEARCHED (Int.Cl. 3)

B 01 J 39/22
C 08 B 3/12
3/24

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	04-01-1980	WENDLING